Langasite SAW Device with Gas-Sensitive Layer

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***Abstract*— High temperature langasite SAW oxygen sensors using ZnO as a resistive sensing layer were fabricated and tested in a wired configuration up to 650 °C, representing an important step toward future high temperature wireless sensor development. ZnO layers deposited by spin coating and RF sputtering methods were compared. The langasite SAW sensor with spin coated ZnO sensing film had strongly increasing surface wave attenuation from 100 °C to 250 °C and undetectable reflections above 250°C. The langasite SAW gas sensor with sputtered ZnO sensing film showed clear oxygen gas flow response from 500 °C to 650 °C.**

***Keywords*-Keyword: surface scoustic wave; langasite; zinc oxide; oxygen sensor; high temperature; sputtering; spin coating**

I. INTRODUCTION

There is increasing demand for gas sensors capable of operating in harsh environments. In particular, high temperature exhaust gas sensors are needed for control of oxy-fuel combustion systems. These sensors will make it possible to control the combustion process so as to achieve a nearly pure carbon dioxide exhaust suitable for geologic sequestration. Wireless operation is desirable to eliminate power and signal transmission cables. However, very few technological options are available for wireless sensing in the temperature range (600°C to 1000°C) of interest. We report here on the development of a high-temperature surface acoustic wave (SAW) oxygen sensor. We consider wired operation only but such sensors can also be operated in wireless mode [1-2].

SAW devices have been extensively studied for sensor applications, including sensing of viscosity, strain, pressure, temperature, and gas concentration [3]. We consider here a SAW gas sensor in which a gas sensitive layer deposited on the propagation path changes conductivity with gas concentration [4]. The variation of sensing layer conductivity changes the surface acoustic wave velocity, which is then measured by RF interrogation equipment.

We use langasite ($La_3Ga_5SiO_{14}$), which has been shown to be a promising substrate for high temperature sensing [5-7] due to its relatively large electromechanical coefficient (0.4%), and high melting temperature (1470 °C). Langasite has been studied for both high temperature bulk acoustic wave (BAW) and surface acoustic wave applications [8-10]. Fritze *et al.* have used langasite microbalance BAW sensors for the detection of O_2 at high temperature [11]. Thiele and da Cunha have reported a langasite SAW H_2 and C_2H_2 gas sensor operating up to 750 °C [12]. This paper reports on high temperature langasite SAW oxygen sensors fabricated and tested in wired mode up to 650 °C, representing an important step toward high temperature wireless sensor development. In this work, we used ZnO as the oxygen resistive sensing layer and explored spin coating and sputtering deposition methods. ZnO is an oxygen defect conductor that decreases in conductivity with increasing oxygen concentration [13]. Our langasite SAW sensor with a sputtered ZnO sensing film showed sensitivity to oxygen gas between 500 °C to 650 °C.

II. LANGASITE SAW GAS SENSOR

We used 76 mm diameter, 0.5 mm thick langasite wafers (Roditi International, UK) with Euler angles (0, 138.5, 27) as the SAW device substrate. Interdigitated transducers (IDTs) were fabricated using a lift-off technique and e-beam sputtering. The IDT metallization consisted of 100 nm or 50 nm platinum with 10 nm titanium as an adhesion layer. SAW sensors with several different combinations of transmitting and reflecting IDTs were designed. Figure 1 shows one typical design, where the transmitter was located in the center, and five reflectors were located on two sides at center-to-center separations of 2.56 mm, 3.2 mm, 3.84 mm, 4.48 mm and 5.44 mm. The transmitter and reflector IDTs had 2 µm finger widths and 1:1 mask to space ratio, yielding an 8 µm surface acoustic wavelength. The transmitter IDTs had 50 electrode finger pairs. The number of electrode finger pairs of reflector IDTs varied from 20 to 60 in different SAW sensor designs. The transmitter and reflector had the same aperture, 50 or 100 wavelengths. The two terminals of each IDT are connected to avoid pyroelectric charge accumulation during fabrication. The shorting lines had very large impedance at the driving frequency, thus the reflectors can be viewed as an open reflector design.

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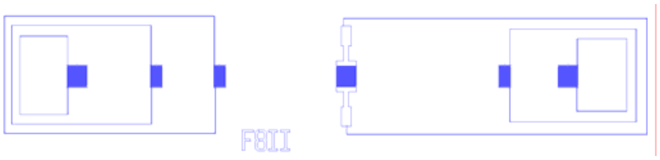

Figure 1. Sensor mask design.

A ZnO/SiO_2/langasite SAW device was first fabricated using the spin coating method, where ZnO is the sensing layer, and SiO_2 is a spacer layer. The langasite SAW device was spin coated with polysiloxanes (IC1-200 and DC4-500 from Futurrex, Inc.) at 2000 rpm. It was then annealed in air at 400 °C for 30 min to form a 200 nm SiO_2 layer. A ZnO layer, ~ 140 nm thick, was then deposited onto the SiO_2/langsite SAW device using the sol-gel spin coating method described in [14]. Briefly, the SAW device was spin-coated using a sol-gel solution containing zinc acetate (1.3 M Zn^{++} concentration) followed by air drying and an air anneal at 700 °C. The ZnO and SiO_2 layers on the IDT transmitter region were partially removed using a cotton tip with acetone to expose the transmitter terminals before each annealing step. A SAW device with only 200 nm SiO_2 was also prepared for comparison.

A ZnO/langasite SAW device was also fabricated using RF sputtering. 200 nm of ZnO was deposited by sputtering from a 2.5 cm diameter Zn target at a pressure of 4 mT, and RF power 50 W, in 25% O_2/ 75% Ar. ZnO was masked from the IDT terminals using Mylar tape.

X-ray diffraction (XRD) measurements were performed using a PANalytical X'Pert ProMPD powder diffractometer with a Cu X-ray source. Figure 2 shows diffraction patterns of 200 nm thick ZnO films sputtered onto a SiO_2-coated Si wafer after annealing at 600°C for 30 min and 750°C for 8 hr, and a ZnO film spin coated (1 coat, 1.3 M) onto a stainless steel substrate and annealed at 700 °C for one hour.

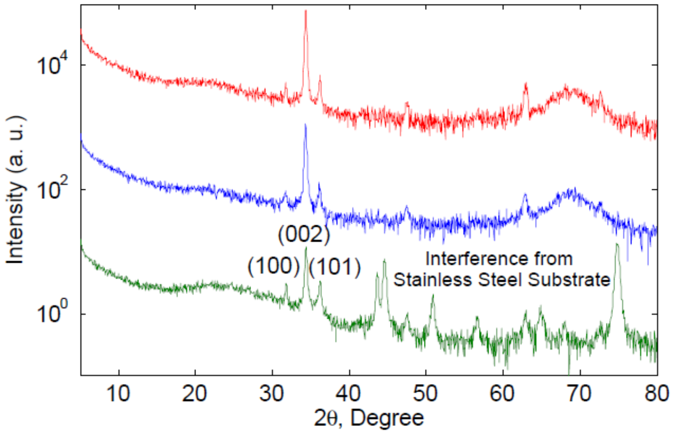

Figure 2. X ray diffraction measurements. 200 nm sputtered ZnO film on SiO_2-coated silicon substrate annealed at 750 °C (red) and 600 °C (blue); 140 nm spin coated ZnO film on stainless steel substrate annealed at 700 °C (green).

All three samples show diffraction features characteristic of the ZnO wurtzite structure: (100) at 31.7°, (002) at 34.4° and (101) at 36.3°, with a strong preference for growth in the (002) (c-axis) direction. The average size of crystalline domains, determined by Scherrer analysis of the (002) feature, is on the order of 30 nm for all three samples. The intensities of the spin-coated sample's diffraction features are lower than those of the corresponding features in the sputtered samples; this difference likely reflects the fact that the spin coated film is thinner.

III. HIGH TEMPERATURE GAS TESTING

For high temperature characterization, a sheathed mineral-insulated thermocouple wire (Omega, Super OMEGACLAD XL) was used as the high temperature RF cable to connect the SAW sensor to the RF measurement equipment (Figure 3). One thermocouple wire is grounded to the tube, while the other wire is used for signal transmission. Thermocouple wire of this type is convenient because it can tolerate high temperatures and exhibits a characteristic impedance near 50 ohms. Platinum/silver paste (9595-A ESL ElectroScience) was used to bond the langasite SAW devices to a 5 cm by 5 cm alumina ceramic substrate. The conducting paste is also used to connect the high temperature RF cable with the SAW IDT transmitter terminals. No impedance matching circuit was used in the high-temperature experiments to simplify the package design.

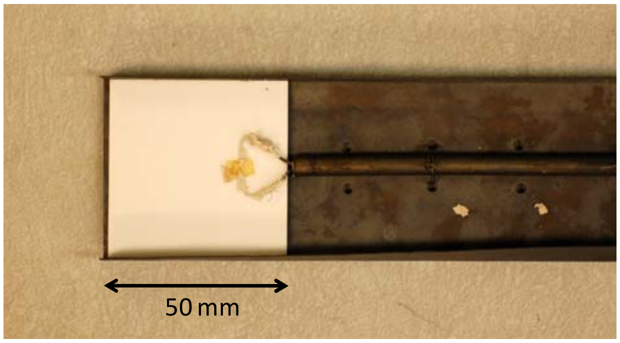

Figure 3. Langasite SAW device connected for wired measurement.

Langasite SAW sensors were placed in a tube furnace for high temperature measurement. One end of the tube furnace is connected to the computer-controlled mass flow controllers, which were used to precisely deliver the targeted O_2/N_2 gas flow rate. The conductivity-based langasite SAW gas sensor requires a high resolution phase measurement to detect a surface acoustic wave velocity change of order 0.01% due to the low electro-mechanical coefficient. In order to achieve this measurement resolution, we used phase detection method to measure surface acoustic wave velocity change, which is described in another paper [10]. Briefly, an RF vector signal generator (NI PXI-5670) and a vector signal analyzer (NI PXI 5661) were used to perform non-coherent phase detection on the reflections using the attenuated excitation pulse as a reference. The change of surface acoustic wave velocity corresponding to different O_2/N_2 concentration was then calculated from phase change measurements, adjusting for the propagation length for different reflections.

IV. RESULTS AND DISCUSSION

Langasite SAW devices with different structures were fabricated and characterized, including bare langasite, spin coated SiO_2/langasite, spin coated ZnO/SiO_2/langasite, and sputtering coated ZnO/langasite SAW devices. The S_{11} parameter of the IDT transmitter was measured on a probe station with a network analyzer (Rhode and Schwartz ZVB 4) at room temperature. The resonant frequencies for bare langasite, spin coated

SiO_2/langasite, and spin coated ZnO/ SiO_2/langasite were all close to 340 MHz, as expected since the IDT transmitter are not covered with any layer. The sputter-coated ZnO/langasite SAW devices, where the IDT transmitter is covered with a ZnO layer, had a resonant frequency of 335 MHz.

The SAW devices were characterized in time domain as a function of temperature as described in Section III. Since the resonant frequency changes with temperature, the excitation frequency was adjusted by searching for the maximum SAW reflection amplitude with varying excitation frequency. The SAW reflections of those devices were recorded at different temperature at the adjusted resonant frequency. Figure 4 shows the time domain response of a sputter-coated ZnO/langasite SAW device at 650 °C, (SAW device design shown in Figure 1). The first and the second SAW reflections arrived at 1.84 and 2.24 µsec, respectively.

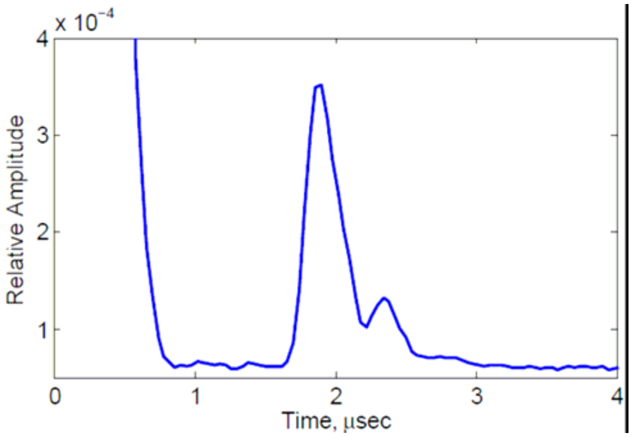

Figure 4. Sputter-coated ZnO/langasite (0, 138.5, 27) SAW sensor reflections at 650 °C. Two reflections were at 1.88, and 2.24 µsec. The peak before 0.8 µsec is leakage from the T/R switch.

For all SAW devices examined, strong reflections were observed at room temperature, and the reflection magnitudes decreased with increasing temperature. Figure 5 shows the comparison of surface acoustic wave attenuation per µsec propagation time as a function of temperature. There was significant SAW attenuation for the spin coated ZnO/SiO_2/langasite SAW devices from 100 °C to 250 °C. Above 250 C the reflections are too small to detect with our measurement system. Comparing the attenuation measurements of spin coated ZnO/SiO_2/langasite and SiO_2/langasite SAW devices, we see that sol-gel spin coated ZnO layer is the major attenuation source.

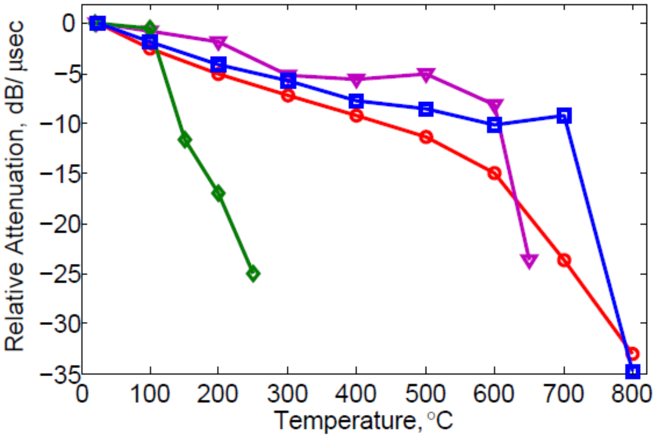

Figure 5. Surface acoustic wave attenuation of different SAW devices as a function of temperature. Blue square □ : non-layered langasite; purple triangle ∇ : sputtering coated ZnO/langasite; red round O: spin coated SiO_2/langasite; green diamond ◊ : spin coated ZnO/SiO_2/langasite.

The SAW reflections from sputter-coated ZnO/langasite and bare langasite SAW devices were observable up to 650 °C and 800 °C respectively. For the bare langasite SAW device, degradation of Pt electrode is likely the reason for device failure around 800 °C as reported in [15]. For the sputter-coated ZnO/langasite device, microscopy after exposure to temperatures up to 700 °C shows a discolored region near the edge of the Pt/Ag paste, suggesting that a reaction occurred with the paste eventually leading to loss of electrical contact (Figure 6).

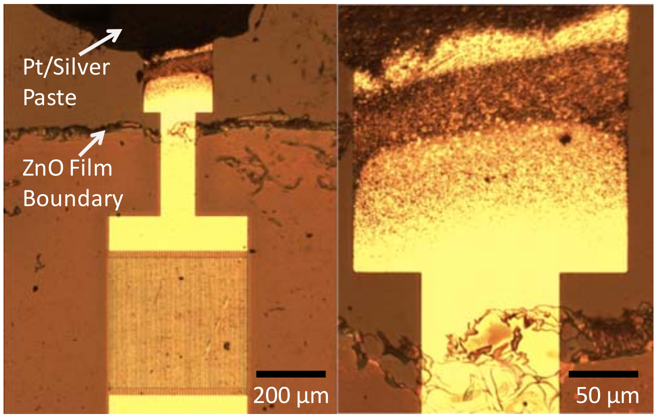

Figure 6. Micrograph of sputter-coated ZnO/langasite SAW device after annealed at 650 °C.

The sputter-coated ZnO/langasite SAW device was tested for O_2 response at temperatures up to 650 °C. 25 sccm O_2 and 975 sccm N_2 was used as the baseline gas flow. The tube furnace is flushed with the baseline gas flow for one hour before each test run to achieve temperature equilibrium in the furnace. The O_2 flow rate was set at 800 sccm, 400 sccm, and 200 sccm for 15 min, with 15 min interval. The total flow rate is kept at 1000 sccm throughout the measurements.

Figure 7 shows the measured phase change per µsec propagation time of the ZnO/langasite SAW device at 500 °C, 600 °C, 650 °C, and a bare langasite SAW device at 600 °C. The bare device exhibits a small phase change that appears to be correlated with the gas flow. This could be due to gas sensitivity of the bare langasite or small temperature variations resulting from slight imbalances in the gas flow. It is known that oxygen partial pressure changes can cause a change in langasite bulk conductivity [11]. However, the phase change caused by the langasite bulk conductivity is 2 orders smaller than phase change observed for the bare langasite SAW device. Therefore, we believe that the phase change is due to temperature variation caused by the unbalanced O_2/N_2 gas flow, given the fact that langasite SAW device is a highly sensitive temperature sensor above 400 °C. Measurements of the temperature inside the tube showed that the temperature varied less than ±1 °C. A ±1 °C temperature variation can only cause a phase change of about 0.11 radians [10]. We therefore conclude that the phase changes in Figure 7 are mostly caused by a change in ZnO sensing film conductivity with oxygen concentration.

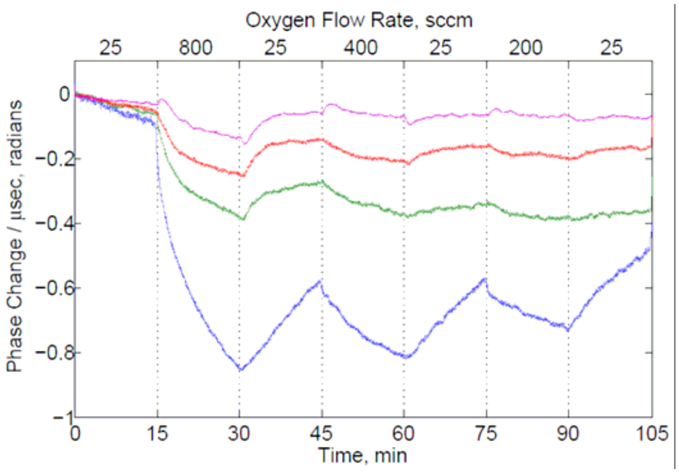

Figure 7. Phase change per µsec propagation time as a function of gas testing time. ZnO/langasite SAW device at 500 °C (red), 600 °C (green), 650 °C (blue), and the bare langasite SAW device at 600 °C (purple).

Figure 7 shows a comparison of the maximum phase change per µsec propagation time as a function of O_2 concentration. The phase change response from the ZnO/langasite gas sensor increases as the temperature increase from 500 °C to 650 °C.

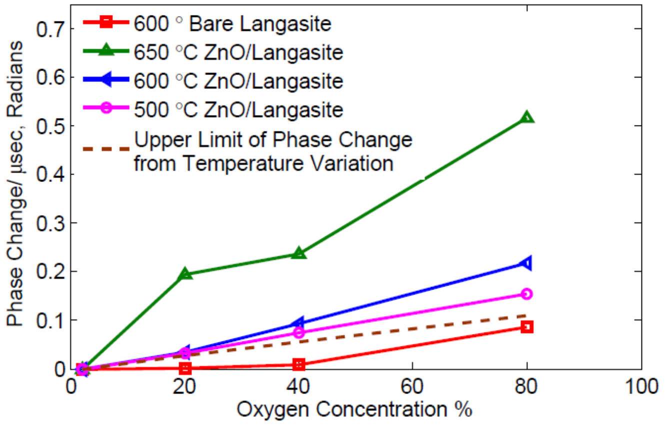

Figure 8. Phase change per µsec propagation time as a function of oxygen concentration in the gas testing.

These phase changes are clearly large compared to the phase change for bare langasite and the phase change potentially resulting from temperature variations due to gas flow. We also note that ZnO is highly insulating at room temperature and the conductivity at constant oxygen concentration is thermally activated. As a result an increasing oxygen response with temperature is expected.

V. CONCLUSION

High temperature langasite SAW oxygen sensors using ZnO as the oxygen-sensing layer were fabricated and tested in a wired configuration up to 650 °C. In this work, we compared ZnO layers deposited by spin coating and RF sputtering. The langasite SAW sensor with spin coated ZnO sensing film exhibited increasing attenuation beginning at 100 °C with no detectable reflections above 250 °C. On the other hand, the SAW device with the sputtered ZnO sensing film had detectable reflections up to 650 C. Phase changes correlated with the oxygen partial pressure were observed between 500 °C and 650 °C. These phase changes were caused by the intended sensing mechanism, namely, oxygen-induced changes in the ZnO conductivity. Operation at higher temperatures is prevented at present by contact failure.

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